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[54]发明名称 掺有多元醇的水硬性水泥促凝剂

[57]摘要

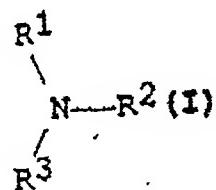
本发明公开了一种用于水硬性水泥组合物的新型促凝外加剂。这些外加剂包含公知的促凝剂和低分子量的多元醇，例如丙三醇和乙二醇，发现这种外加剂对水硬性水泥，砂浆和混凝土的初凝时间的缩短有神奇的功效，而且作为低温促凝剂也是有利的。本发明优选的实施方案还可包括选自于某些链烷醇胺和它们的混合物的成分。

1. 一种缩短包含有水硬性水泥胶结剂，水泥组合物凝固时间的外加剂，所述外加剂包括：

a) 选自于以下组成的促凝剂成分：碱金属或碱土金属硝酸盐，亚硝酸盐，和甲酸盐；第七族卤素和假卤素酸的碱金属或碱土金属盐；碱金属或碱土金属的硫代硫酸盐或高氯酸盐，碱金属或碱土金属铝酸盐，硅酸盐，和氢氧化物，和它们的混合物；

b) 定义为2-6个碳的脂族二元醇和三元醇的C₂-C₆多元醇成分，其存在量有效地增加促凝剂成分的促凝性能。

c) 选自于链烷醇胺和它们的混合物的成分，所说的链烷醇胺具有的通式为



其中，R¹和R²是羟烷基，R³是氢，羟烷基，或烷基。

2. 权利要求1的外加剂，其中在所说的外加剂中的所说的多元醇的用量大约为0.05-40% (重量)，它以所说的外加剂中多元醇成分和促凝剂成分的总重量为基。

3. 权利要求1的外加剂，其中在所说的外加剂中的所说的多元醇成分的用量大约为2.0-30% (重量)，它以所说的外加剂中多元

醇成分和促凝剂成分的总重量为基。

4. 权利要求1的外加剂，其中所述的促凝剂成分是有机酸或无机酸的碱金属或碱土金属盐，或它们的混合物。

5. 权利要求1的外加剂，其中所述的促凝剂成分选自于硝酸钙，亚硝酸钙，和它们的混合物。

6. 权利要求5的外加剂，其中R³是甲基，乙基，丙基，异丙基，丁基，异丁基，戊基或异戊基。

7. 权利要求5的外加剂，其中R³是甲基，乙基，丙基，或异丙基。

8. 权利要求7的外加剂；其中R¹和R²是羟甲基，羟乙基，羟丙基，羟异丙基，或羟丁基。

9. 权利要求3的外加剂，其中在所说的外加剂中的所说的成分c)的用量大约0.1-6.0% (重量)，它以所说的外加剂中所有活性固体成分的总重量为基。

10. 权利要求3的外加剂，其中在所说的外加剂中的所说的成分c)的量大约是1.0-5.0% (重量)，它以所说的外加剂中所有活性固体成分的总重量为基。

11. 权利要求3的外加剂，其中在所说的外加剂中的所说的成分c)的大约是2.0-4.0% (重量)，它以所说的外加剂中的所有活性固体成分的总重量为基。

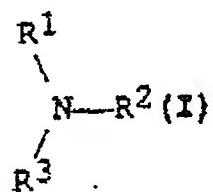
12. 权利要求1的外加剂，其中所说的C₂-C₆的多元醇成分选自于乙二醇，二甘醇，丙二醇，和丙三醇。

13. 用于缩短包含水硬性水泥胶结剂的水泥组合物凝固时间的外加剂，所说的外加剂主要组成是

a) 选自于碱金属 或碱土金属硝酸盐；亚硝酸盐， 和甲酸盐的促凝剂成分；

b) 定义为2-6个碳的脂族二元醇和三元醇的C₂- C₆的多元醇成分， 存在的有效地增加促凝剂成分的促凝性能；

c) 选自于链烷醇胺和它们的混合物的成分， 所说的链烷醇胺通式为，



其中R¹和R²是羟烷基， R³是氢， 羟烷基， 或烷基； 和

d) 第七族卤素和假卤素酸的碱金属和碱土金属盐； 碱金属或碱土金属硫代硫酸盐和高氯酸盐； 碱金属或碱土金属铝酸盐， 硅酸盐， 和氢氧化物； 和它们的混合物。

14. 权利要求13的外加剂， 其中R³是甲基， 乙基， 丙基， 异丙基， 丁基， 异丁基， 戊基和异戊基。

15. 权利要求13的外加剂， 其中R³是甲基， 乙基， 丙基， 或异丙基。

16. 权利要求13的外加剂， 其中R¹和R²是羟甲基， 羟乙基， 羟丙基， 羟异丙基， 或羟丁基。

17. 权利要求13的外加剂， 其中在所说的外加剂中的所说的成分c) 的量大约是0.1-6.0% (重量)， 它以在所说的外加剂中的所有活性固体成分的总重量为基。

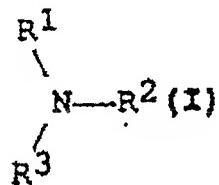
18. 权利要求13的外加剂，其中在所说的外加剂中的所说的成分d)的量大约是1.0-5.0% (重量)，它以在所说的外加剂中的所有活性固体成分的总重量为基。

19. 一种水泥组合物，它包含有水硬性水泥胶结剂和

a) 选自于以下组成的促凝剂成分；碱金属或碱土金属硝酸盐，亚硝酸盐，和甲酸盐；第七族卤素和假卤素酸的碱金属或碱土金属盐；碱金属或碱土金属硫代硫酸盐和高氯酸盐；碱金属或碱土金属铝酸盐，硅酸盐，和氢氧化物；和它们的混合物；

b) 定义为2-6个碳的脂族二元醇和三元醇的C₂-C₆多元醇成分，存在的量有效地增加促凝剂成分的促凝性能；

c) 选自于链烷醇胺和它们的混合物的成分，所说的链烷醇胺通式为：



其中R¹和R²是羟烷基，R³是氢，羟烷基，或烷基。

20. 权利要求19的水泥组合物，其中在所说的外加剂中的所说的C₂-C₆多元醇成分的量大约是0.05-40% (重量)，它以在所说的外加剂中多元醇成分和促凝剂成分的总重量为基。

21. 权利要求19的水泥组合物，其中在所说的外加剂中的所说的C₂-C₆多元醇成分的量大约是2.0-30% (重量)，它以在所说的外加剂中的多元醇成分和促凝剂成分的总重量为基。

22, 权利要求19的水泥组合物，其中所说的促凝剂成分是有机或无机酸的碱金属或碱土金属盐，或它们的混合物。

23, 权利要求19的水泥组合物，其中所述的促凝剂成分选自于硝酸钙，亚硝酸钙，和它们的混合物。

24, 权利要求23的水泥组合物，其中R³是甲基，乙基，丙基，异丙基，丁基，异丁基，戊基或异戊基。

25, 权利要求23的水泥组合物，其中R³是甲基，乙基，丙基，或异丙基。

26, 权利要求24的水泥组合物，其中R¹和R²是羟甲基，羟乙基，羟丙基，羟异丙基，或羟丁基。

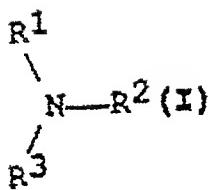
27, 权利要求19的水泥组合物，其中所说的C₂-C₆的多元醇成分选自于乙二醇，二甘醇，丙二醇，和丙三醇。

28, 制备含有水硬性水泥胶结剂的水泥组合物的方法，所说的方法包括向所说的水泥组合物中加入

a) 选自于下列组成的促凝剂成分：碱金属或碱土金属硝酸盐，亚硝酸盐，和甲酸盐；第七族卤素和假卤素酸的碱金属或碱土金属盐；碱金属或碱土金属的硫代硫酸盐和高氯酸盐；碱金属或碱土金属铝酸盐，硅酸盐和氢氧化物；和它们的混合物。

b) 定义为2-6个碳的脂族二元醇和三元醇的C₂-C₆多元醇成分，其存在的量应有效地增加促凝剂成分的促凝性能；

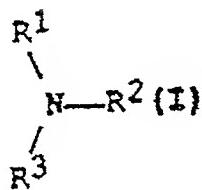
c) 选自于链烷醇胺和它们的混合物的成分，所说的链烷醇胺通式为，



其中R¹和R²是羟烷基，R³是氢，羟烷基，或烷基。

29. 用于缩短含有水硬性水泥粘结剂的水泥组合物的凝固时间的阻止腐蚀，促凝剂， 所说的外加剂包括以下组成的促凝剂成分：

- a) 选自于碱金属或碱土金属硝酸盐，亚硝酸盐，和甲酸盐；第七族卤素和假卤素酸的碱金属或碱土金属的盐； 碱金属或碱土金属硫代硫酸盐和高氯酸盐； 碱金属或碱土金属铝酸盐，硅酸盐，和氢氧化物； 和它们的混合物；
- b) 定义为2-6个碳的脂族二元的和三元醇的C₂-C₆多元醇成分，其存在的量有效地增加促凝剂成分的促凝性能；
- c) 选自于链烷醇胺和它们的混合物的成分， 所说的链烷醇胺通式为，



其中R¹和R²是羟烷基，R³是氢，羟烷基，或烷基。

掺有多元醇的水硬性水泥促凝剂

本申请是1993年4月9日提出的未决美国申请08/046,110, 的部分后续申请，而08/046, 110又是现在已放弃的于1992年1月28日提出的美国申请07/827, 196, 的后续申请，它的全部公开内容在此引入作为参考。

本发明涉及用于水硬性水泥组合物如砂浆，水泥浆和混凝土的改进促凝剂。更具体的说，本发明涉及新型促凝剂和採用添加某些低分子量的多元醇如丙三醇，乙二醇和二甘醇来加速凝固的方法。

当需要在冻结或接近冻结的温度下使用水硬性水泥组合物时，应使用促凝剂。例如，温度对波特兰水泥的水化速度有很大影响，比如，低温时，波特兰水泥组合物硬化速度一般比要求的慢，除非加速硬化过程。除了加速凝固外，也希望在正常的或低温下能够增加早期强度的发展速度。这样能缩短达到混凝土规定强度的养护和保护所必需的时间。加速凝固的一些技术是：增加拌合料中水泥的比例，加热拌合料，和应用作为拌合料成分的化学外加剂及增加水泥浆的凝固速度。

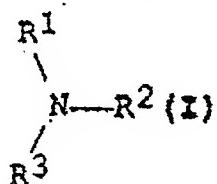
一些化学促凝剂是众所周知的。它们包括碱金属氢氧化物，硅酸盐，氟硅酸盐，甲酸钙；氯化钠，氯化钙；和硝酸钙和亚硝酸钙。

氯化钙因为其制备容易和廉价以及它对水泥的影响能够预测并有许多文献资料而被广泛地应用。然而类似于氯化钠，它有腐蚀钢筋的缺点。这样；它能导致混凝土中增强钢筋的腐蚀。应用氯化钙的其它缺点包括降低后期抗压强度，降低对加气剂的响应，致使硬化的混凝土表面起疱(Concrete Admixtures, Dodson: van Nostrand Reinhold, 1990)。

于是，本发明的目的是提供新型的促凝剂，它能在低温时缩短水硬性水泥组合物的凝固时间，而不会引起或加速增强水泥钢筋的腐蚀。

本发明的另一个目的是提供制备这类水泥组合物方法和提供缩短水硬性水泥组合物凝固时间的方法。

本发明涉及新型水硬性水泥促凝剂组合物，也涉及含有这类外添加剂的水泥组合物和所述水泥组合物的制备方法。外添加剂组合物包括促凝剂组分和以有效量存在增加促凝剂成分促凝性能的C₂-C₆的多元醇。本发明还涉及制备水硬性水泥组合物的方法，其方法包括向包括水硬性水泥胶结剂的水泥组合物中加入促凝剂成分，和以有效量存在的增加促凝剂成分促凝性能的C₂-C₆多元醇成分。本发明也涉及包含水硬性水泥胶结剂，促凝剂成分，和以有效量存在的增加促凝剂成分促凝性能的C₂-C₆的多元醇成分的水泥组合物。本发明一个优选的实施方案还包括选自于链烷醇胺和它们的混合物的成分。这样的链烷醇胺具有的通式是：



其中R¹和R²是羟烷基，并且R³是氢，羟烷基，或烷基。本发明特别优选的一个实施方案的主要组成为a) 碱金属或碱土金属亚硝酸盐；b) C₂-C₆的多元醇成分(如本文定义)，其存在的量能有效地增加促凝剂成分的促凝性能；c) C₁-C₅的烷基二乙醇胺和它们的混合物；和d) 氯化钙，溴化物，碘化物，氯化物，氟酸盐，叠氮化物，硫氟酸盐，硫代硫酸盐或高氯酸盐。

已经发现，包括促凝化合物和低分子量的多元醇的外加剂对于缩短水硬性水泥组合物的凝固时间有优异的特效。还发现这样的外加剂在低的工作温度下即低于约50°F也特别有效。很显然这些低分子量多元醇增加了促凝化合物的促凝性能。此外，本发明的外加剂可以这种方式配制，即所生成的组合物会阻止一般埋置在水泥组合物中的增强钢筋的腐蚀。

本文所用的术语“多元醇”是指2-6个碳，即“C₂-C₆”脂族的二元醇或三元醇。适用于本发明的多元醇是如乙二醇，二甘醇，丙二醇和丙三醇的物质。满足以上定义的其它化合物对于专业技术人员来说是显而易见的。到目前为止，还不知道这些化合物具有任何促凝特性，即它们最初是当作助磨剂和缓凝剂使用。由于这个原因，人们并没有意识到这些化合物具有作为部分促凝剂的任何价值。令发明者吃惊的是本文所描述的多元醇与促凝剂化合物共同应用时，与把单独的促凝剂加入到水泥组合物中所获得的促凝相比，其显著地增加了水泥组合物的促凝。这样本发明使用多元醇成分得到了水泥组合物的促凝包括所需的“辅助”促凝。

本文所用的术语“水泥组合物”指的是水泥浆，砂浆和混凝土组合物，它包括水硬性水泥胶结剂。上述术语是技术术语。

水泥浆是由水硬性水泥胶结剂例如波特兰水泥，单独或与粉煤灰、硅灰或高炉矿渣结合，和水组成的混合物；砂浆是另外包括细集料的水泥浆，和混凝土是另外包括粗骨料的砂浆。这类组合物还可另外包括其它添加物如消泡剂，引气剂或消气剂，缓凝剂，减水剂，超塑化剂和其它现有技术中公知的用于改变组合物特性的那些外添加剂。本发明的水泥组合物的配制是通过将要求量的某些材料，如水硬性水泥，水，细或粗骨料混合，它可用作特种水泥组合物。

促凝剂成分可以是任何化合物，当其加到水泥组合物中（如上所述）时，能缩短水泥组合物硬化所需要的时间。例如，可使用的碱金属或碱土金属盐是有机或无机酸的盐。尽管以下目录并不意味着限制。但这样化合物的例子是碱金属或碱土金属硝酸盐，亚硝酸盐，和甲酸盐；第七族卤素和假卤素酸的碱金属或碱土金属盐，比如，碱金属或碱土金属氯化物，溴化物，碘化物，氟化物，氯酸盐，叠氮化物，和硫氰酸盐；碱金属或碱土金属硫代硫酸盐和高氯酸盐；和碱金属或碱土金属铝酸盐，硅酸盐，和氢氧化物，比如氢氧化钠。钙盐是特别好的，特别是硝酸钙，氯化钙，甲酸钙，和亚硝酸钙。

应用碱金属或碱土金属盐的混合物也是可行的，例如，硝酸钙和亚硝酸钙的混合物。所用的盐之间的比例可以是任意的；可使用的优选的硝酸钙/亚硝酸钙的混合物，其重量比例范围大约是1:3-3:1。发明人发现应用硝酸钙/亚硝酸钙混合物作为促凝剂成分的这类外添加剂有利于阻止普遍埋设在水泥组合物中的增强钢筋的腐蚀。

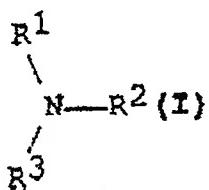
如果将促凝剂成分和多元醇成分分别加入到水泥组合物中，所加入的多元醇，以固体为基的固体百分量（“% S/S”）一般大约是0.05%-1.0% S/S（以水泥组合物中水硬性水泥胶结剂的重量为基），优选的范围是大约0.1%-0.75% S/S，这样的浓度一般能提供人们所希望的对凝固的加速。促凝剂成分可以以对促凝所必须的常用量加入，但是一般大约在0.05%-4.0% S/S的范围。（注意，通过应用本发明的多元醇成分，还可减少一般要求达到一定促凝水平的促凝剂成分的数量，这是因为通过多元醇和促凝剂的结合提供了较好的促凝作用。）

然而，本发明人发现，在将多元醇成分和促凝剂成分加入到水泥组合物中之前，优选的是将它们与按要求的量化合。这样只需要计量出一种组合物并加入到水泥组合物中。这比单独加入各种成分的方法简单且更准确并且减少了配制正确配方的错误机会。

如果促凝剂成分和多元醇成分在加入到水泥组合物之前进行混合，多元醇成分和促凝剂成分可接任何比例有效地结合以获得所要求的结果。一般，混合物中多元醇的量可以是大约0.5-40%（重量）（以多元醇成分和促凝剂成分的总重量为基），优选的是大约2-30%（重量）。

应将本发明的外加剂以有效量地混合到水硬性水泥组合物中，使之达到要求的凝固。外加剂的单位用量能够容易确定并且将取决于水泥组合物，组合物中各成分的比例，和所希望的凝固程度。一般，加入到水泥组合物中的外加剂的量（正如以上所说）所提供的多元醇的浓度大约是0.05%-1.0% S/S，优选的是约0.1-0.75% S/S，一般这样的浓度对凝固能产生所希望的加速。

本发明特别优选的实施方案还包括选自于链烷醇胺和它们的混合物的成分。这样的链烷醇胺的通式是



其中R¹和R²是羟烷基，R³是氢，羟烷基，或烷基。羟烷基优选的是C₁-C₄羟烷基，例如羟甲基，羟乙基，羟丙基，羟异丙基，或羟丁基，更优选的是C₁-C₃羟烷基。R³优选的是C₁-C₅烷基例如甲基，乙基，丙基，异丙基，丁基，异丁基，戊基，或异戊基，更优选的是C₁-C₃烷基。特别优选的链烷醇胺是C₁-C₅烷基二乙醇胺(即，R³是C₁-C₅的烷基比如甲基)比如是甲基二乙醇胺，或乙基二乙醇胺。

加入这样的外添加剂成分，令人吃惊地发现，所提供的水泥硬化体具有的抗压强度比不包含本发明实施方案的水泥硬化体高。此外，在特别优选的本发明的实施方案中主要组成是，a) 碱金属或碱土金属亚硝酸盐；b) C₂-C₆多元醇成分(如本文定义)，其存在量能有效地增加促凝剂成分的促凝性能；c) C₁-C₅的烷基二乙醇胺和它们的混合物；d) 氯化钙，溴化物，碘化物，氟化物，氰酸盐，叠氮化物，硫氰酸盐，硫代硫酸盐或高氯酸盐，这样，甚至能够获得更高的抗压强度。因为众所周知卤化物，假卤化物对埋置在混凝土中的增强钢筋有腐蚀，而与此同时，却发现应用本发明特别优选实施方案能阻止水泥硬化体中的腐蚀，这是非常令人

吃惊的。还有，对于水泥硬化体，本发明令人吃惊地表现出能增加所有养护龄期的抗压强度。

一般，本发明外添加剂中链烷醇胺的用量可以是大约0.1-6.0% (重量) (以外添加剂中所有活性固体成分的总重量为基)，优选的大约是1.0-5.0% (重量)，更优选的是大约2.0-4.0% (重量)。如果分别加入到水泥组合物中，所加的外加成分(以固体为基的固体百分含量)大约是0.005%-0.10% S/S (以水泥组合物中的水硬性水泥胶结剂为基)，优选的范围大约是0.01%-0.08% S/S。在此段所描述的特别优选的本发明实施方案中，外添加剂成分d)的用量可以是大约0.5-15.0% (重量) (以外添加剂中所有活性固体总重量为基)，更优选的是大约3.0-6.0% (重量)。

本发明的外添加剂可按类似于现有技术中任何传统的方式被加入到水泥组合物中。外添加剂应当与水泥组合物非常均匀地混合。

给出以下实施例仅起说明的目的，除非另外指明，所有的份数和比例都以重量计。

实施例1

制备由硝酸钙和亚硝酸钙组成，比例为2:1，于水中的外添加剂。外添加剂的总固体量是42.6%。

实施例2

制备组成为由硝酸钙，亚硝酸钙，和丙三醇组成，比例为2:1:1，(重量)，于水中的外添加剂。外添加剂总固体量是45%。

实施例3

将实例1和实例2中所制备的外添加剂分别加入砂浆中，砂浆是用I-II型波特兰水泥，砂子制备的，水灰比为0.45。同时也制备

不含外添加剂的空白砂浆。每份砂浆是通过把4500g砂子，900g H₂O，和2000g水泥在Hobart搅拌机中机搅拌均匀而制得。加入足够量的实施例1，和2的外添加剂溶液以使外添加剂固体浓度为0.5% S/S，和2.0% S/S（以混合物中的水硬性水泥重量为基）。凝固时间按照ASTMC403测定，测定时的温度为55°F。

表1的数据表明以不同的加入量加入本发明的多元醇成分（丙三醇），在硝酸钙和亚硝酸钙混合物的情况下改进了速凝剂化合物性能。

实施例4

制备由硝酸钙，亚硝酸钙和丙三醇组成比例为 60:16:24（重量），于水中的本发明外添加剂。外添加剂总固体量是45%。

实施例5

将在实施例4中制备的外添加剂加入到砂浆中，砂浆是用三种不同的I-II型波特兰水泥（“水泥1，2，和3”），砂子制得的，水灰比为0.45，还用各种水泥制备不含外添加剂的空白砂浆。每份砂浆是通过把4500g砂子，900g水，和2000g水泥在Hobart 搅拌机中混合均匀而制得。加入实施例4 的足够量的外添加剂溶液以提供固体浓度为2.5% S/S的外添加剂（以混合物中水硬性水泥的重量为基）。凝固时间按照ASTMC403测定。测定时的温度是40°F。

表2的结果表明三种水泥类型的凝固时间的特性。数据说明本发明速凝水泥外添加剂的低温特性。

实施例中的外加剂	初凝时间(小时)	初凝时间变化(小时)
	11.08	
(空白)	11.08	
1 (at 0.5% s/s)	8.94	2.14
2 (at 0.5% s/s)	7.97	3.11
1 (at 2.0% s/s)	5.05	6.03
2 (at 2.0% s/s)	3.74	7.34

表2 初凝时间(小时)

实施例中的外加剂	水泥1	水泥2	水泥3	平均
	9.50	11.40	10.18	10.36
4	7.57	8.57	6.33	8.16

实施例5

按照本发明最优选的实施方案按表3制备，于水中的外加剂。所有的数据是以外加剂中所有活性固体成分的总重量为基的外加剂各成分的重量百分比。

表3

	样品1	样品2	样品-3a	样品-3b	样品-3c
Ca(NO ₂) ₂	43.9	42.0	42.0	41.8	38.3
Ca(NO ₃) ₂	43.7	42.0	42.0	41.8	38.3
二甘醇	10.0	8.0	9.5	8.0	8.0
甲基二乙醇胺	-	6.0	6.0	3.0	3.0
萘磺酸盐甲醛 缩聚物	2.4	2.0	0.5	0.4	4.0
CaBr ₂	-	-	-	5.0	12.0

实施例6

在与实施例3相似的条件下，用五种实验室用水泥测定外加剂SA-1和SA-2的特性。混合温度是60°F并且砂浆在40°F下硬化。示于表4的数据清楚地说明含有本发明链烷醇胺的外加剂产生了良好的7-28天抗压强度。

表4

			抗压强度(psi)		
	凝固时间(小时.分钟)	oz/cwt [†]	2-3天	7天	28天
对比	13.67	-	880	2270	3330
SA-1	10.05	30.0	1020	2450	3720
SA-2	10.15	30.0	840	2610	3840

+液量磅外添加剂/100lbs水泥

实施例7

含有不同量的碱土金属卤化物(溴化钙), SA-3b和SA-3C, 的外添加剂的性能用象实施例6那样的三种实验室用水泥进行测定。混合温度是72°F并且水泥在20°F下硬化。如表5所示, 另外加入CaBr很明显对改善早期抗压强度(3天)有利; 这样, 加入这种外添加剂到混凝土中, 增加了所有养护期的抗压强度。

表5

			抗压强度(psi)	
	凝固时间(小时.分钟)	oz/cwt	3天	28天
对比	不凝固(冻结)		.	.
SA-3a	5.49	75	262	4041
SA-3b	4.06	75	588	5060
SA-3c	4.78	75	701	4494

本发明前面的描述是为了说明本发明而不是为了限制本发明。本发明人指出在所附权利要求的范围之内的各种修改或变化均不违背本发明的精神。

Hydraulic cement set-accelerators incorporating polyols

This application is a continuation-in-part of pending U.S. application Ser. No. 08/046,110, filed on Apr. 9, 1993, which is a continuation of U.S. application Ser. No. 07/827,196, filed on Jan. 28, 1992, now abandoned, the entire disclosures of which are incorporated herein by reference.

This invention relates to improved set-accelerators for hydraulic cement compositions such as mortars, grouts and concretes. More particularly the invention relates to novel set-accelerators and methods for set-acceleration employing the addition of certain low molecular weight polyols, e.g., glycerol and ethylene and diethylene glycol.

Set accelerators are used when it is necessary to work with hydraulic cement compositions at freezing or near-freezing temperatures. The rate of hydration of Portland cement, for example, is very dependent on temperature, such that, at lower temperatures, Portland cement compositions will often harden at a rate slower than desired unless the hardening process is accelerated. In addition to accelerating the set, it is desirable to also attain an increase in the rate of early strength development at normal or low temperatures. This reduces curing and protection periods necessary to achieve specified strengths in concrete. Some techniques for accelerating the set are: increasing the proportion of cement in the mix, heating the mix, and using chemical admixtures that act on the components of the mix to increase the rate at which the cement paste sets.

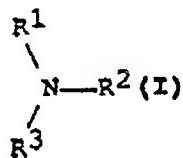
Several chemical set accelerators are well-known. They include alkali hydroxides, silicates, fluorosilicates, calcium formate, sodium chloride, calcium chloride, and calcium nitrate and calcium nitrite.

Calcium chloride is widely used because it is easy and inexpensive to produce and its effects on hydraulic cement are predictable and well-documented. However, like sodium chloride, it has the disadvantage of corroding steel. Thus, it can cause the corrosion of steel reinforcing bars in concrete. Other drawbacks of calcium chloride use include reduced compressive strength at later ages, reduced response to air entrainment, and blotching of hardened concrete surfaces (Concrete Admixtures, Dodson: Van Nostrand Reinhold, 1990).

It is thus an object of this invention to provide new set-accelerators which reduce the set time of hydraulic cement compositions at lower temperatures, without inducing or promoting corrosion of steel reinforcement.

Further objects of the invention are to provide methods for preparing such cement compositions and to provide methods for reducing the set time of hydraulic cement compositions.

This invention is directed toward new hydraulic cement set-accelerators compositions, to cement compositions containing such admixtures, and to methods for preparing said cement compositions. The admixture compositions comprise a set accelerator component and a C₂-C₆ glycol component present in an amount effective to increase the set acceleration properties of the set-accelerator component. The invention further relates to a method of making a hydraulic cement composition comprising adding to a cement composition comprising a hydraulic cement binder, a set-accelerating component, and a C₂ to C₆ polyol component in an amount effective to increase the set-acceleration properties of the set-accelerator component, and to a cement composition comprising a hydraulic cement binder, a set-accelerating component, and a C₂ to C₆ polyol component present in an amount effective to increase the set acceleration properties of the set-accelerator component. A preferred embodiment of the invention further comprises a component selected from the group consisting of alkanolamines and mixtures thereof. Such alkanolamines are of the formula:



where R¹ and R² are hydroxyalkyl groups, and R³ is either hydrogen, a hydroxyalkyl group, or an alkyl group. A particularly preferred embodiment of the invention consists essentially of a) an alkali or alkaline earth metal nitrite; b) a C₂ to C₆ polyol component (as defined herein) that is present in an amount effective to increase the set acceleration properties of the set-accelerator component; c) C₁ to C₅ alkyl diethanolamines and mixtures thereof; and d) calcium chloride, bromide, iodide, cyanide, cyanate, azide, thiocyanate, thiosulfate or perchlorate.

It has been found that admixtures comprising a set-accelerating compound and low molecular weight polyols are surprisingly effective in reducing the set time of hydraulic cement compositions. Such admixtures are also found to be quite effective at lower working temperatures, i.e., below about 50 °F. It appears that these low molecular weight glycols increase the set-acceleration properties of a set-accelerating compound. Additionally, admixtures of this invention may be formulated in such a way as to produce a composition that will inhibit corrosion in steel reinforcing bars commonly embedded in cement compositions.

The term "glycol" as used herein is intended to mean two to six carbon, i.e., "C₂ to C₆", aliphatic di- and trihydric alcohols. Polyols suitable for use in the invention are those such as ethylene glycol, diethylene glycol, propylene glycol, and glycerol. Other compounds meeting the above definition will be apparent to those skilled in the art. Until now these compounds have not been known to have any set-accelerating qualities, i.e., they have been used primarily as grinding aids and set retarders. For

this reason these compounds were not seen as having any value as part of a set-accelerating admixture. As such it was surprising to the inventors that a glycol as described herein could be used with a set-accelerating compound to significantly increase the set acceleration of a cement composition over that obtained by the addition of the set accelerator alone to the cement composition. Thus this invention utilizes the polyol component to give the set acceleration of the cement composition containing the set accelerator a desired "boost."

The term "cement composition" as used herein refers to pastes, mortars and concrete compositions comprising a hydraulic cement binder. The above terms are terms of art. Pastes are mixtures composed of a hydraulic cement binder, for example, Portland cement, either alone or in combination with fly ash, silica fume or blast furnace slag, and water; mortars are pastes additionally including as fine aggregate, and concretes are mortars additionally including coarse aggregate. Such compositions may additionally include other admixtures such as defoaming agents, air-entraining or detraining agents, set retarders, water reducing agents, superplasticizers, and other components known to those in the art for altering properties of the composition. The cement compositions of this invention are formed by mixing required amounts of certain materials, e.g., a hydraulic cement, water, and fine or coarse aggregate, as may be applicable for the particular cement composition being formed.

The set-accelerating component may be any compound which, when added to a cement composition (as described above), reduces the amount of time required for the cement composition to harden. For example, an alkali or alkaline earth metal salt which is a salt of an organic or inorganic acid may be employed. Although the following list is not meant to be limiting, examples of these compounds are alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VII halogen and pseudohalogen acids, such as alkali or alkaline earth metal chloride, bromide, iodide, cyanide, cyanate, azide, and thiocyanate; alkali or alkaline earth metal thiosulfate and perchlorate; and alkali or alkaline earth metal aluminates, silicates, and hydroxides, e.g., sodium hydroxide. Calcium salts are particularly advantageous, especially calcium nitrate, calcium chloride, calcium formate, and calcium nitrite.

It is also feasible to use a mixture of alkali or alkaline earth metal salts, for example, a mixture of calcium nitrate and calcium nitrite. Any ratio of the salts used may be employed; in a preferred calcium nitrate/calcium nitrite mixture, a range of weight ratios of from about 1:3 to 3:1 may be used. The inventors have found that such an admixture, using a calcium nitrate/calcium nitrite mixture as the set-accelerator component, is beneficial in inhibiting corrosion in steel reinforcing bars commonly imbedded in cement compositions.

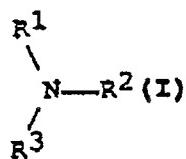
If the set-accelerating component and polyol component are added to the cement composition separately, the polyol may be added, generally, in percent solids on

solids ("% s/s"), in the range of about 0.05% s/s to 1.0% s/s (based on the weight of hydraulic cement binder in the cement composition), with a preferred range of about 0.1% s/s to 0.75% s/s, such concentrations being generally those which provide the desired boost in acceleration. The set-accelerating component may be added in the usual amounts necessary for set-acceleration, but generally in a range of from about 0.05% s/s to about 4.0% s/s. (Note that through the use of a polyol component of the invention, it is also possible to reduce the amount of set-accelerator component normally required for a certain level of set acceleration, because of the better set-acceleration provided by the combination of the polyol and the set-accelerator.)

However, the inventors find it is preferable to combine the polyol component and the set-accelerating component in desired amounts before addition to a cement composition, so only one composition need be metered out and added to the cement composition. This is a simpler and more precise method than adding each component separately and reduces the opportunity for error in dispensing the correct formulation. If the set-accelerating component and polyol component are to be mixed before addition to a cement composition, the polyol component and the set-accelerating component may be combined in any proportion effective to give the desired results. Generally, the amount of the polyol in the mixture may range from about 0.5 to 40 weight % (based on the combined weight of polyol component and accelerator component), and preferably from about 2 to 30 weight %.

An admixture of the invention should be mixed into a hydraulic cement composition in an amount effective to allow the acceleration desired. The specific amount of the admixture can be readily determined and will depend on the cement composition, the ratio of components of the composition, and the degree of acceleration desired. The admixture is generally added to a cement composition in an amount which, as noted above, provides a polyol concentration of from about 0.05% s/s to 1.0% s/s, preferably from about 0.1% s/s to 0.75% s/s, such concentrations being generally those which provide the desired boost in acceleration.

A particularly preferred embodiment of the invention further comprises a component selected from the group consisting of alkanolamines and mixtures thereof. Such alkanolamines are of the formula



where R^1 and R^2 are hydroxyalkyl groups, and R^3 is either hydrogen, a hydroxyalkyl group, or an alkyl group. The hydroxyalkyl group(s) are preferably C₁ to C₄ hydroxyalkyl, e.g., hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxyisopropyl, or hydroxybutyl, and more preferably C₁ to C₃ hydroxyalkyl. R^3 is preferably a C₁ to C₅ alkyl group, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl or

isopentyl, and more preferably a C₁ to C₃ alkyl. Particularly preferred alkanolamines are C₁ to C₅ alkyl diethanolamines (i.e., R³ is a C₁ to C₅ alkyl group such as methyl), such as methyl or ethyl diethanolamine.

The addition of this additional component, surprisingly, has been found to provide hardened cement objects with greater compressive strengths than those cements not containing this embodiment of the invention. What is more, in a particularly preferred embodiment of the invention consisting essentially of a) alkali or alkaline earth metal nitrite; b) a C₂ to C₆ polyol component (as defined herein) that is present in an amount effective to increase the set acceleration properties of the set-accelerator component; c) C₁ to C₅ alkyl diethanolamines and mixtures thereof; and d) calcium chloride, bromide, iodide, cyanide, cyanate, azide, thiocyanate, thiosulfate or perchlorate, even higher compressive strengths may be achieved. This is particularly surprising because while halides or pseudohalides are well-known to be corrosive to steel reinforcing bars embedded in the concrete, the use of the particularly preferred embodiment of the invention is actually found to inhibit corrosion in the hardened cement object. Furthermore, the invention is seen to surprisingly provide for cement objects having increased compressive strength at all curing stages.

Generally, the amount of the alkanolamine component in an admixture of the invention may range from about 0.1 to 6.0 weight % (based on the total weight of all active solid components in the admixture), preferably from about 1.0 to 5.0 weight %, and more preferably from about 2.0 to 4.0 weight %. If added to the cement composition separately, the additional component may be generally added, in percent solids on solids, in the range of about 0.005% s/s 0.10% s/s (based on the weight of hydraulic cement binder in the cement composition), with a preferred range of about 0.01% s/s to 0.08% s/s. In the particularly preferred embodiment of the invention described in this paragraph, in an admixture the amount of component d) may be from about 0.5 to 15.0 weight % (based on the total weight of all active solid components in the admixture), more preferably from about 3.0 to 6.0 weight %.

The admixtures of this invention can be added to cement compositions in any conventional manner familiar to those in the art. The admixture should be substantially uniformly mixed with the cement composition.

The following examples are given for illustrative purposes only. Unless otherwise indicated, all parts and proportions are by weight.

EXAMPLE 1

An admixture was prepared consisting of calcium nitrate and calcium nitrite, in a 2:1 ratio, in water. The total % solids of the admixture was 42.6%.

EXAMPLE 2

An admixture of the invention was prepared consisting of calcium nitrate, calcium nitrite, and glycerol, in a 2:1:1 ratio (by weight), in water. The total % solids of the admixture was 45%.

EXAMPLE 3

The admixtures prepared in Examples 1 and 2 were each added individually to mortars prepared using a Type I-II Portland cement, sand, and a water to cement ratio of 0.45. A blank mortar, containing no admixture, was also prepared. Each mortar was prepared by combining 4500 g of sand, 900 g of H₂O, and 2000 g of cement in a Hobart mixer until homogeneous. A sufficient amount of the admixture solutions of Examples 1 and 2 was added to provide an admixture solid concentration of 0.5% s/s, and 2.0% s/s (based on the weight of hydraulic cement in the admixture). Set times were measured in accordance with ASTM C403. The test was performed at 55 °F.

Table 1 presents the data, which demonstrate, at different addition amounts, the utility of adding a polyol component of the invention (glycerol), to improve the performance of a set-accelerating compound, in this case a mixture of calcium nitrate and calcium nitrite.

EXAMPLE 4

An admixture of the invention was prepared consisting of calcium nitrate, calcium nitrite and glycerol, in a proportion of 60:16:24 (by weight), in water. The total % solids of the admixture was 45%.

EXAMPLE 5

The admixture prepared in Example 4 was added to mortars prepared using three different Type I-II Portland cements ("Cements 1, 2, and 3"), sand, and a water to cement ratio of 0.45. Blank mortars, containing no admixture, were also prepared with each cement. Each mortar was prepared by combining 4500 g of sand, 900 g of H₂O, and 2000 g of cement in a Hobart mixer until homogeneous. A sufficient amount of the admixture solution of Example 4 was added to provide an admixture solids concentration of 2.5% s/s (based on the weight of hydraulic cement in the admixture). Set times were measured in accordance with ASTM C403. The test was performed at 40 °F.

Table 2 presents the results, which show the set time performance with the three cement types. The data demonstrate the cold-temperature performance of a set accelerating cement admixture of the invention.

TABLE 1

Admixture of Example #	Initial Set Time (hr)	Change In Initial Set Time(hr)
blank	11.08	—
1 (at 0.5% s/s)	8.94	2.14
2 (at 0.5% s/s)	7.97	3.11
1 (at 2.0% s/s)	5.05	6.03
2 (at 2.0% s/s)	3.74	7.34

TABLE 2

Admix of Example #	Initial Set Time (hr)			
	Cement 1	Cement 2	Cement 3	Avg.
blank	9.50	11.40	10.18	10.36
4	7.57	8.57	8.33	8.16

EXAMPLE 5

Admixtures in accordance with more preferred embodiments of the invention were prepared, in water, according to Table 3. All numbers are the weight % of each component in the admixture based on the total weight of all active solid components in the admixture.

TABLE 3

	SA-1	SA-2	SA-3a	SA-3b	SA-3c
Ca(NO ₂) ₂	43.9	42.0	42.0	41.8	38.3
Ca(NO ₃) ₂	43.7	42.0	42.0	41.8	38.3
diethylene glycol	10.0	8.0	9.5	8.0	8.0
methyldiethanolamine	-	6.0	6.0	3.0	3.0
naphthalene sulfonate	2.4	2.0	0.5	0.4	4.0
formaldehyde condensate					
CaBr ₂	-	-	-	5.0	12.0

EXAMPLE 6

The performance of admixtures SA-1 and SA-2 were evaluated with five laboratory cements under conditions similar to that in Example 3. The mix temperature was 60 °F and the mortars were hardened at 40 °F. The data shown in Table 4 clearly demonstrate the better 7-28 day compressive strengths imparted by the admixture containing the alkanolamines of the invention.

TABLE 4

Set time (hr. min)	Oz/cwt ⁺	Compressive Strength (psi)		
		2-3 day	7 day	28 day
Control	13.67	-	880	2270
SA-1	10.05	30.0	1020	2450
SA-2	10.15	30.0	840	2610
			3330	3720
			3840	

⁺fluid ounces admixture/100 lbs cement

EXAMPLE 7

The performance of admixtures containing various amounts of an alkaline earth metal halide (calcium bromide), SA-3b and SA-3c, were evaluated with three laboratory cements as in Example 6. The mix temperature was 72 °F. and the cement was hardened at 20 °F. As seen in Table 5, the further addition of CaBr is clearly beneficial in improving the early (3 day) compressive strength; thus the addition of such admixtures to concrete provides an increase in compressive strength at all curing stages.

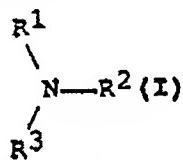
TABLE 5

Set time (hr. min)	Oz/cwt ⁺	Compressive Strength (psi)	
		3 day	28 day
Control	did not set (froze)	-	-
SA-1	5.49	75	262
SA-2	4.06	75	588
SA-3	4.78	75	701
			4041
			5060
			4494

The preceding description of the invention has been intended to illustrate rather than limit the invention. The inventors intend that various modifications or changes be made within the scope of the appended claims without departing from the spirit of the invention.

Claims

1. An admixture for reducing the set time of a cement composition which contains a hydraulic cement binder, said admixture comprising
 - a) a set-accelerator component selected from the group consisting of alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VII halogen and pseudohalogen acids; alkali or alkaline earth metal aluminates, silicates, and hydroxides; and mixtures thereof; and
 - b) a C₂ to C₆ polyol component which is defined as a two to six carbon aliphatic di- and trihydric alcohol, present in an amount effective to increase the set acceleration properties of the set-accelerator component.
 - c) a component selected from the group consisting of alkanolamines and mixtures thereof, said alkanolamines having the formula



where R¹ and R² are hydroxyalkyl groups, and R³ is either hydrogen, a hydroxyalkyl group, or an alkyl group.

2. The admixture of claim 1 wherein the amount of said polyol component in said admixture is in the range of from about 0.05 to 40 weight %, based on the combined weight of polyol component and accelerator component in said admixture.
3. The admixture of claim 1 wherein the amount of said polyol component in said admixture is in the range of from about 2.0 to 30 weight %, based on the combined weight of polyol component and accelerator component in said admixture.
4. The admixture of claim 1 wherein said set-accelerating component is selected from the group consisting of an alkali or alkaline earth metal salt of an organic or inorganic acid, and mixtures thereof.
5. The admixture of claim 1 wherein said set-accelerating component is selected from the group consisting of calcium nitrate, calcium nitrite, and mixtures thereof.
6. The admixture of claim 5 wherein R³ is methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl or isopentyl.
7. The admixture of claim 5 wherein R³ is methyl, ethyl, propyl or isopropyl.
8. The admixture of claim 5 wherein R¹ and R² is hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxyisopropyl, or hydroxybutyl.

9. The admixture of claim 3 wherein the amount of said component c) in said admixture is in the range of from about 0.1 to 6.0 weight %, based on the total weight of all active solid components in said admixture.

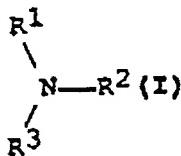
10. The admixture of claim 3 wherein the amount of said component c) in said admixture is in the range of from about 1.0 to 5.0 weight %, based on the total weight of all active solid components in said admixture.

11. The admixture of claim 3 wherein the amount of said component c) in said admixture is in the range of from about 2.0 to 4.0 weight %, based on the total weight of all active solid components in said admixture.

12. The admixture of claim 1 wherein said C₂ to C₆ polyol component is selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, and glycerol.

13. An admixture for reducing the set time of a cement composition which contains a hydraulic cement binder, said admixture comprising

- a) a set-accelerator component selected from the group consisting of alkali or alkaline earth metal nitrate, nitrite, and formate;
- b) a C₂ to C₆ polyol component which is defined as a two to six carbon aliphatic di- and trihydric alcohol, present in an amount effective to increase the set acceleration properties of the set-accelerator component;
- c) a component selected from the group consisting of alkanolamines and mixtures thereof, said alkanolamines having the formula



where R¹ and R² are hydroxyalkyl groups, and R³ is either hydrogen, a hydroxyalkyl group, or an alkyl group; and

d) alkali or alkaline earth metal salts of Group VII halogen and pseudohalogen acids; alkali or alkaline earth metal thiosulfate and perchlorate; alkali or alkaline earth metal aluminates, silicates, and hydroxides; and mixtures thereof;

14. The admixture of claim 13 wherein R³ is methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl or isopentyl.

15. The admixture of claim 13 wherein R³ is methyl, ethyl, propyl or isopropyl.

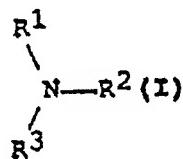
16. The admixture of claim 13 wherein R¹ and R² is hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxyisopropyl, or hydroxybutyl.

17. The admixture of claim 13 wherein the amount of said component c) in said admixture is in the range of from about 0.1 to 6.0 weight %, based on the total weight of all active solid components in said admixture.

18. The admixture of claim 13 wherein the amount of said component c) in said admixture is in the range of from about 1.0 to 5.0 weight %, based on the total weight of all active solid components in said admixture.

19. A cement composition comprising a hydraulic cement binder and

- a) a set-accelerator component selected from the group consisting of alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VII halogen and pseudohalogen acids; alkali or alkaline earth metal aluminates, silicates, and hydroxides; and mixtures thereof; and
- b) a C₂ to C₆ polyol component which is defined as a two to six carbon aliphatic di- and trihydric alcohol, present in an amount effective to increase the set acceleration properties of the set-accelerator component.
- c) a component selected from the group consisting of alkanolamines and mixtures thereof, said alkanolamines having the formula



where R¹ and R² are hydroxyalkyl groups, and R³ is either hydrogen, a hydroxyalkyl group, or an alkyl group.

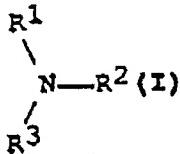
20. The cement composition of claim 19 wherein the amount of said C₂ to C₆ polyol component in said admixture is in the range of from about 0.05 to 40 weight %, based on the combined weight of polyol component and accelerator component in said admixture.

21. The cement composition of claim 19 wherein the amount of said C₂ to C₆ polyol component in said admixture is in the range of from about 2.0 to 30 weight %, based on the combined weight of polyol component and accelerator component in said admixture.

22. The cement composition of claim 19 wherein said set-accelerating component is selected from the group consisting of an alkali or alkaline earth metal salt of an organic or inorganic acid, and mixtures thereof.

23. The cement composition of claim 19 wherein said set-accelerating component is selected from the group consisting of calcium nitrate, calcium nitrite, and mixtures thereof.

24. The cement composition of claim 23 wherein R³ is methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl or isopentyl.
25. The cement composition of claim 23 wherein R³ is methyl, ethyl, propyl or isopropyl.
26. The cement composition of claim 24 wherein R¹ and R² is hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxyisopropyl, or hydroxybutyl.
27. The cement composition of claim 19 wherein said C₂ to C₆ polyol component is selected from the group consisting of ethylene glycol, diethylene glycol, propylene glycol, and glycerol.
28. A method for making a cement composition which contains a hydraulic cement binder, said method comprising adding to said cement composition
 a) a set-accelerator component selected from the group consisting of alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VII halogen and pseudohalogen acids; alkali or alkaline earth metal thiosulfate and perchlorate; alkali or alkaline earth metal aluminates, silicates, and hydroxides; and mixtures thereof;
 b) a C₂ to C₆ polyol component which is defined as a two to six carbon aliphatic di- and trihydric alcohol, present in an amount effective to increase the set acceleration properties of the set-accelerator component.
 c) a component selected from the group consisting of alkanolamines and mixtures thereof, said alkanolamines having the formula

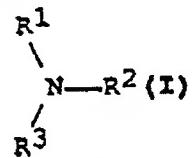


where R¹ and R² are hydroxyalkyl groups, and R³ is either hydrogen, a hydroxyalkyl group, or an alkyl group.

29. A corrosion-inhibiting, set-accelerating admixture for reducing the set time of a cement composition which contains a hydraulic cement binder, said admixture comprising
 a) a set-accelerator component selected from the group consisting of alkali or alkaline earth metal nitrate, nitrite, and formate; alkali or alkaline earth metal salts of Group VII halogen and pseudohalogen acids; alkali or alkaline earth metal thiosulfate and perchlorate; alkali or alkaline earth metal aluminates, silicates, and hydroxides; and mixtures thereof;
 b) a C₂ to C₆ polyol component which is defined as a two to six carbon aliphatic di- and trihydric alcohol, present in an amount effective to increase the set acceleration

properties of the set-accelerator component.

c) a component selected from the group consisting of alkanolamines and mixtures thereof, said alkanolamines having the formula



where R¹ and R² are hydroxyalkyl groups, and R³ is either hydrogen, a hydroxyalkyl group, or an alkyl group.

Abstract

New set-accelerating admixtures for hydraulic cement compositions are disclosed. These admixtures incorporate known set accelerators and low molecular weight polyols, e.g., glycerol and ethylene glycol, are found to be surprisingly effective in decreasing the initial set time of hydraulic cements, mortars, and concretes, and are also advantageous as reduced-temperature set-accelerators. Preferred embodiments of the invention may also comprise a component selected from the group consisting of certain alkanolamines and mixtures thereof.